

Polymer Chemistry

THE BASIC CONCEPTS

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The resulting radical is stabilized by electron delocalization and eventually reacts with either another inhibitor radical by combination (dimerization) or disproportionation or with an initiator or other radical.

Molecular oxygen contains two unpaired electrons and has the distinction of being capable of both initiating and inhibiting polymerization. It functions in the latter capacity by forming the relatively unreactive peroxy radical:



Inhibitors are characterized by inhibition constants which are defined as the ratio of the rate constant for transfer to inhibitor to the propagation constant for the monomer in analogy with Eq. (6.87) for chain transfer constants. For styrene at 50°C the inhibition constant of *p*-benzoquinone is 518, and that for O_2 is 1.5×10^4 . *The Polymer Handbook* (Ref. 3) is an excellent source for these and most other rate constants discussed in this chapter.

6.9 Techniques of Polymerization: Emulsion Polymerization

A number of chain-growth polymers are commercially produced on a high tonnage basis, and the technology of polymerization deserves some comment even though it is not our main emphasis in this volume. Many important monomers polymerize with the evolution of large amounts of heat. This can result in temperature increases, increased kinetic constants, and accelerated reaction rates—in short, to runaway reactions—unless the heat is dissipated. Many important monomers are toxic, carcinogenic, or both and hence must be processed carefully for the safety of workers in the industry and users of the products. These facts, plus the diversity of monomers employed and the assortment of end uses for polymer products, make the choice of a polymerization technique a highly specific matter. In this section we shall discuss some of the possibilities.

Several polymerization techniques are in widespread usage. Our discussion is biased in favor of methods that reveal additional aspects of addition polymerization and not on the relative importance of the methods in industrial practice. We shall discuss four polymerization techniques: bulk, solution, suspension, and emulsion polymerization.

Bulk and solution polymerizations are more or less self-explanatory since they operate under the conditions we have assumed throughout most of this chapter. A bulk polymerization may be conducted with as few as two components: monomer and initiator. Production polymerization reactions are carried out to high conversions which produces several consequences we have mentioned previously:

Techniques of Polymerization: Emulsion Polymerization

1. The rate process for termination is hindered through the Trommsdorff effect.
2. Because of the decrease in R_i , R_p and \bar{P} increase as the percent conversion increases.
3. This produces even greater increases in viscosity, with the attendant increase in the difficulty of heat removal and processing.
4. Very strong stirring equipment is needed for mixing because of the high viscosity, and long tubular reactors with low cross-sectional area are needed for heat exchange.
5. Use of chain transfer agents may be indicated to regulate \bar{P} and thus avoid some of the difficulties mentioned in items (3) and (4).

* Solution polymerization is the name given to the technique of polymer formation in the presence of a solvent. The polymer may not have the same solubility in the solvent as the monomer, so the system may become heterogeneous with the formation of polymer. Although there is an increase in viscosity as polymer concentration in the system increases, the effect is mitigated by the presence of solvent, and autoacceleration through the Trommsdorff mechanism is less troublesome than in bulk polymerizations. This permits easier stirring and better heat exchange than in the bulk. The solvent is ordinarily chosen to show low chain transfer so that high molecular weight polymer is obtained. Solvent recovery must be considered as part of the overall process and this, of course, adds to the cost of this method.

A technique called suspension polymerization is sometimes employed with water-insoluble monomers. In this procedure the monomer is suspended by agitation as small drops in an aqueous medium. The diameters of the drops are in the range of micrometers to millimeters in this technique. Coalescence of the monomer drops is prevented by stirring and by addition of water-soluble polymers like gelatin or by suspending clay particles like kaolin in the mixture. Oil-soluble initiators are used so that each monomer drop behaves as a miniature bulk polymerization system. The advantage of suspension polymerization is the ease of heat removal, and a disadvantage is the need to separate the polymer from the suspending medium and wash it free of additives. Suspension polymerization is also called pearl polymerization because of the appearance of the polymer produced.

The fourth and most interesting of the polymerization techniques we shall consider is called emulsion polymerization. It is important to distinguish between suspension and emulsion polymerization, since there is a superficial resemblance between the two and their terminology has potential for confusion. A suspension of oil drops in water is called an emulsion. Water-insoluble monomers are used in the emulsion process also, and the polymerization is carried out in the presence of water; however, the following significant differences also exist:

1. Water-soluble initiators are used.
2. Polymerization occurs in particles whose dimensions are in the nanometer size range, perhaps 10^3 times smaller than the particles in suspension polymerization.
3. Emulsifying agents which are soaps or detergents play a central role in the emulsion polymerization process.
4. The kinetics of polymerization are considerably different from those we have considered elsewhere in this chapter.

These differences have been extensively researched and their origin is quite well understood. We shall present only an abbreviated discussion of the topic, however.

Before we examine the polymerization process itself, it is essential to understand the behavior of the emulsifier molecules. This class of substances is characterized by molecules which possess a polar or ionic group or head and a hydrocarbon chain or tail. The latter is often in the 10–20 carbon atom size range. Dodecyl sulfate ions, from sodium dodecyl sulfate, are typical ionic emulsifiers. These molecules have the following properties which are pertinent to the present discussion:

1. They are water soluble because of the polar head, if one assumes that the tail is not too long.
2. They lower the free energy of an interface between water and some other phase—for example, with air or hydrocarbon—by concentrating in the surface region. At the surface they may be visualized as having their polar heads in the water and their hydrophobic “water-fearing” tails in the other phase. This is called adsorption; such materials are said to be surface active and are also called surfactants. The role of these materials in washing and laundering applications is a consequence of their adsorption behavior.
3. At low concentrations surfactant molecules adsorbed at the surface are in equilibrium with other molecules in solution. Above a threshold concentration, called the critical micelle concentration (cmc, for short), another equilibrium must be considered. This additional equilibrium is that between individual molecules in solution and clusters of emulsifier molecules known as micelles.
4. When micelles are formed just above the cmc, they are spherical aggregates in which surfactant molecules are clustered, tails together, to form a spherical particle. At higher concentrations the amount of excess surfactant is such that the micelles acquire a rod shape or, eventually, even a layer structure.

Figure 6.9 represents schematically the formation of a micelle by the association of n surfactant molecules. The cutaway view of the spherical micelle shows the hydrocarbon interior of these particles. Incidentally, it is this sort of reversible

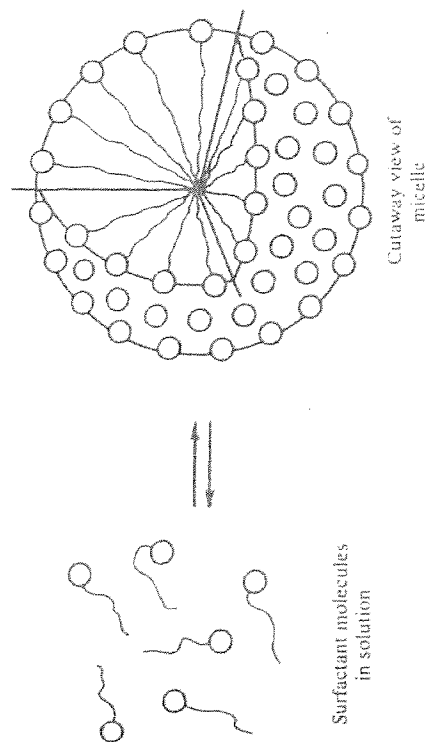


Figure 6.9 Schematic illustration of the micellization process. Cutaway view of spherical micelle shows hydrocarbon interior with polar heads on surface.

association between molecules that was once thought to hold polymers together before covalent structures were accepted.

With this picture in mind, let us consider what happens when monomer is stirred into a surfactant solution which also contains a water-soluble initiator above the cmc.

The surfactant is initially distributed through three different locations: dissolved as individual molecules or ions in the aqueous phase, at the surface of the monomer drops, and as micelles. The latter category holds most of the surfactant. Likewise, the monomer is located in three places. Some monomer is present as individual molecules dissolved in the water. Some monomer diffuses into the oily interior of the micelle, where its concentration is much greater than in the aqueous phase. This process is called solubilization. The third site of monomer is in the dispersed droplets themselves. Most of the monomer is located in the latter, since these drops are much larger, although far less abundant, than the micelles. Figure 6.10 is a schematic illustration of this state of affairs during emulsion polymerization.

Polymerization begins in the aqueous phase with the decomposition of the initiator. The free radicals produced initiate polymerization by reacting with the monomers dissolved in the water. The resulting polymer radicals grow very slowly because of the low concentration of monomer, but as they grow they acquire surface active properties and eventually enter micelles. There is a possibility that they become adsorbed at the oil–water interface of the monomer

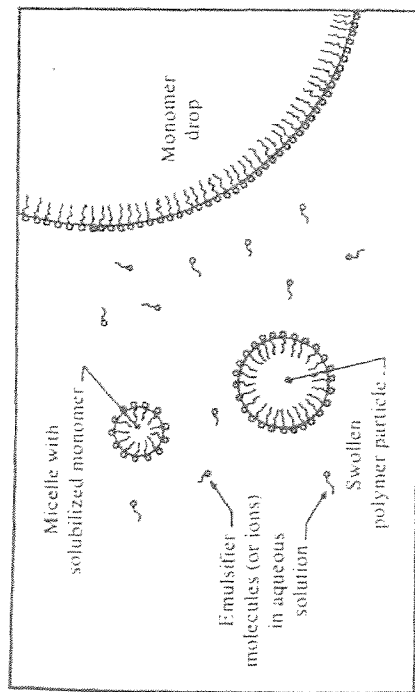


Figure 6.10 Schematic representation of the distribution of surfactant in an emulsion polymerization. Note the relative sizes of suspended particles. [From J. W. Vanderhoff, E. B. Brauford, H. L. Tarkowski, J. B. Shaffer, and R. M. Wiley, *Adv. Chem.* 34:35 (1962).]

drop, but this fate is inconsequential because the micelles are numerically so much more abundant. Once a radical enters a micelle, it polymerizes rapidly, since the concentration of solubilized monomer in the micelle is high. As this overall process continues, there is a general flux of monomer from the droplets to the micelles. The latter expand at the expense of the former. In fact, a micelle that is the locus of polymer growth is rapidly disrupted by the formation of polymer, so that it is no longer appropriate to even consider it a micelle. It is more accurate to consider it a polymer particle swollen by unreacted monomer, with the whole thing covered by adsorbed surfactants. There is a redistribution of surfactant as the polymerization progresses, with more adsorbed on polymer and less on monomer drops. The number of micelles also decreases, since this is the primary reservoir for surfactant.

It takes an initial period—stage one of the process—to get these various processes balanced out; but, after this first stage, polymerization progresses according to a straightforward pattern. We shall continue discussing only the stage which is analogous to a stationary state. The general flux of free radicals is from the aqueous phase into the micelle-swollen polymer particles, of which there are N^* per unit volume in a particular experiment. The entry of the first radical into a micelle initiates the formation of a polymer chain; the arrival of a second radical terminates chain growth. A third radical entering a given particle will initiate a second chain, the fourth radical terminates its growth, and so

on. Within one of these particles, then, there is either zero or one growing chain at any time. Since the entry of radicals into particles is random, there is a 50:50 chance that any one of the N^* micelle-swollen polymer particles is the site of polymer growth at any given moment. In other words, the rate of polymerization is proportional to half the concentration of such particles, $N^*/2$. The rate of polymerization in the second stage of emulsion polymerization, R_p^* , also depends on the concentration of monomer in the micelle $[M^*]$, so we can write

$$R_p^* = k_p [M^*] \left[\frac{N^*}{2} \right] \quad (6.94)$$

The kinetic chain length in emulsion polymerization \bar{p}^* is also readily derived by considering what happens in a single particle. The rate of propagation within a single particle is given by $k_p [M^*]$, while the rate of termination is identical to the rate at which radicals enter the micelle-swollen polymer particle. This, in turn, is equal to the rate of initiation of radicals divided by N^* under second-stage reaction conditions. Therefore the kinetic chain length is

$$\bar{p}^* = \bar{n}_n^* = \frac{k_p [M^*]}{R_i/N^*} = \frac{k_p [M^*] [N^*]}{2fk_d [I]} \quad (6.95)$$

This also gives \bar{n}_n^* , because the small terminating radical has essentially no effect on the degree of polymerization.

It is informative to compare Eqs. (6.94) and (6.95) with Eqs. (6.26) and (6.37), their counterparts for bulk polymerization. In the latter $R_p \propto [M][I]^{1/2}$, while $\bar{p} \propto [M][I]^{-1/2}$. Thus, if an initiator concentration were chosen to produce a predetermined value of \bar{p} , the rate would also be locked in to a particular value. Increasing $[I]$ to increase R_p would have a deleterious effect on the molecular weight of the product. By contrast, in emulsion polymerization, the rate of polymerization is independent of the initiator concentration. Both R_p^* and \bar{p}^* depend on the number of micelle-swollen polymer particles in the second stage of the reaction, but this is primarily governed by the nature and concentration of the surfactant, the temperature, and the concentration of electrolytes which affect the cmc. In emulsion polymerization it is possible to achieve both high rates of polymerization and high degrees of polymerization without being caught in the inverse dependence on $[I]$ that characterizes bulk polymerization. The contrast in these behaviors is illustrated quantitatively by the following example:

Example 6.6

In an emulsion polymerization experiment at 60°C the number of micelles per unit volume is $5.0 \times 10^{15} \text{ liter}^{-1}$ and the monomer concentration in the micelle